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OZONE MEASUREMENTS IN RURAL AREAS,(U)
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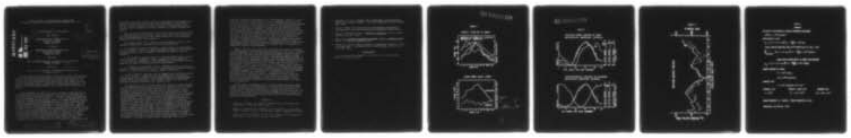

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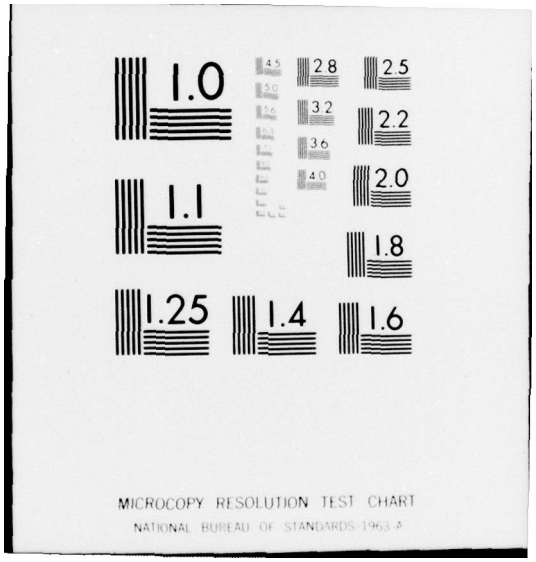
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MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

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Tropospheric Composition, Hollywood, Florida, November 10-12, 1976

OZONE MEASUREMENTS IN RURAL AREAS

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Ozone measurements made at several surface stations in New York and Massachusetts show typical continental diurnal variation; a mountaintop (850 mb) station in the same region experiences very little diurnal variation. The mountaintop ozone concentration always exceeds that of the surface stations, and this concentration trend is predictable by meteorological analysis. The results of these experiments indicate that the ozone source level lies above 850 mb.

Vertical profiles of ozone mixing ratio, averaged to remove the fluctuations, are consistent with a net production in the upper stratosphere and a net destruction at the earth's surface.[1,2] From this results an average background concentration for the "natural" ozone. Ozone concentrations which far exceed this average, and which are not caused by a sudden increase in downward transport, are caused by photochemical production of ozone in the lower part of the troposphere from precursor gases of anthropogenic origin. Downward transport of ozone from the stratosphere to the troposphere occurs when the boundary between the stratosphere and the troposphere deforms, becomes vertical in the core of the jet stream, and then folds beneath the jet core. Danielsen[3] concluded after completing several case studies of large-scale cyclogenesis that "tropopause folding" was an integral part of cyclogenesis and that, therefore, the net seasonal and annual transport of mass could be estimated by multiplying the mass transport per cyclogenesis times the number of cyclogenetic events. This estimate of 4.3×10^{20} gm·year^{-1} implied that a mass

comparable to the entire northern hemispheric stratosphere was exchanged in one year, the outflow being from the lower stratosphere on the cyclonic side of the jets, the inflow implied at higher elevations on the anticyclonic side of the jets. Table 1 summarizes the current estimates on globally averaged ozone fluxes.[4]

Taba[5] reviewed the WMO Congress on ozone observations, which concluded that in a major portion, daily and seasonal variations in ozone concentrations were due to meteorological phenomena. More recent reviews of the ozone literature (Vassy,[6] Reiter[7]) support this conclusion.

It is quite obvious that the average ozone concentration observed in the planetary boundary layer is governed by more than one mechanism:

a. Cyclogenetic events and subsequent further transport of stratospheric air to the ground. (Depends on season and geographic latitude as far as the jet stream is concerned, and on atmospheric stability with regard to vertical transport.)

b. Photochemical production within the planetary boundary layer or in the lowest troposphere. (Depends on season, geographic latitude, atmospheric stability and, most importantly, on the concentration of anthropogenic precursor gases such as oxides of nitrogen and reactive hydrocarbons.)

c. Destruction on the earth's surface. (Depends strongly on the type of surfaces. Values between 0.01 to 2 $cm \cdot s^{-1}$ have been found for surface destruction rates; i.e., they can differ by a factor as high as two hundred.)

It can be expected, therefore, that the average ozone concentration differs from region to region. Background ozone measurements within the planetary boundary layer for the purpose of establishing realistic air quality standards must be made on a regional basis. The "region" is defined by climatology, geographic latitude, topography, type of surface, etc.

The Atmospheric Sciences Research Center and the New York State Department of Environmental Conservation have collaborated in operating a series of ozone observations in rural and urban New York State for several years. Station descriptions can be found in Coffey and Stasiuk.[8] This analysis of ozone background concentration will be confined to the ASRC Whiteface Mt. (4860 ft.) and Schenectady County Airport stations, the Pittsfield, Mass. station operated by the Department of Public Health, Commonwealth of Massachusetts, and the Albany-Rensselaer station operated by the N.Y.S. Department of Environmental Conservation. The secular variation of ozone (1974 data) for these four stations is presented in Figure 1. The data are consistent with the classical concept of increased ozone transport from the stratosphere to the troposphere during the spring ("springtime rise" of ozone). Further mixing down to the ground is enhanced during the summer months, as indicated by the increase in afternoon mixing height measured at the Albany Airport (Fig. 1). A positive correlation between afternoon mixing height and ozone concentration suggests ozone transport from aloft into the planetary boundary layer. It is also interesting to note that the monthly averaged ozone concentration for Whiteface Mt. (4860 ft. or 850 mb) was always highest (except March 1974 for the

Pittsfield station, however, March is not a "photochemical" month") of all the stations. To further substantiate the transport mechanism from aloft as the main source of ozone for this region (versus the photochemical mechanism observed in other regions), we have plotted the "normalized" ozone diurnal in Figure 2 for the four stations. Also plotted in Figure 2 are the normalized diurnal variation of (horizontal) windspeeds. Maximum wind speed results in maximum vertical mixing. Both the ozone concentration and the wind speed peak at 15:00 for the surface stations Rensselaer and Pittsfield and show otherwise an identical trend. The Mountain station has a considerably lower diurnal variation (~13%) and a second ozone maximum at 22:00. This can be explained by the specific local mountain micro meteorology (heating and cooling of the mountain resulting in katabatic wind situations). The diurnal variation of ozone is consistent with the "classical" concept of ozone destruction at the surface and replenishment from aloft, whereby the ozone downward flux to the surface is enhanced as turbulent mixing increases.

Figure 3 shows the mean hourly ozone concentrations observed at Whiteface Mt. and Schenectady County Airport during the period 21-31 July 1975. The 850 mb potential temperatures from the NOAA radiosonde at Albany Airport are noted on the same axis. This short data run is used to facilitate display of hourly values; daily or twice daily means suppress some important short-term trends in ozone concentration. Examination of Figure 3 shows an unmistakable parallel in the trends in ozone concentration at Whiteface Mt. (altitude ~850 mb) and in the 850 mb potential temperature reported for Albany, some 120 miles south of Whiteface Mt. At this level, an increase in air temperature (and/or potential temperature) would be indicative of subsiding air. A warming trend should then be accompanied by increasing ozone concentration, and a cooling trend should be accompanied by steady, or decreasing, ozone concentration. This is the general case for the Whiteface Mt. observations. It is again obvious that the Schenectady ozone concentration appears to approach, but never exceeds, the Whiteface Mt. ozone concentration. For the northeastern region of New York State, we can therefore reiterate the importance of meteorological mixing processes as the dominant parameter governing the diurnal behavior of surface ozone concentrations.

We have further substantiated these findings through occasional airplane flights (equipped with chemiluminescence ozone detectors) over New York State to levels up to 12,000 ft. While the source of ozone observed at the four stations must be "uniformly" distributed at elevated levels (certainly above the 850 mb level and therefore above the planetary boundary layer), we cannot yet establish a link between ozone-rich stratospheric air mass intrusions and high surface ozone concentrations.

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Acknowledgment

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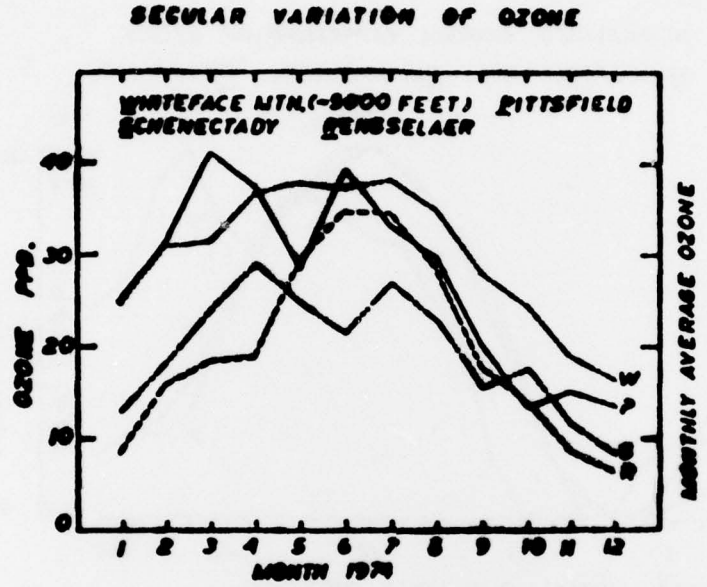
Figure 1



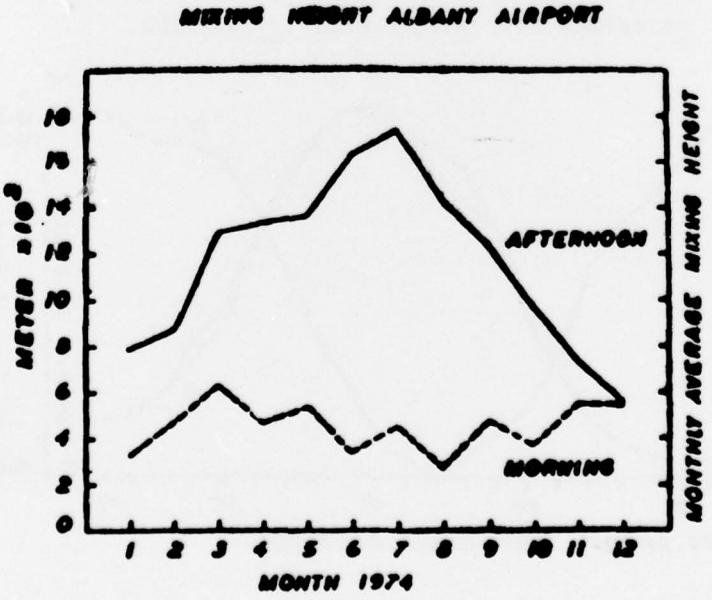
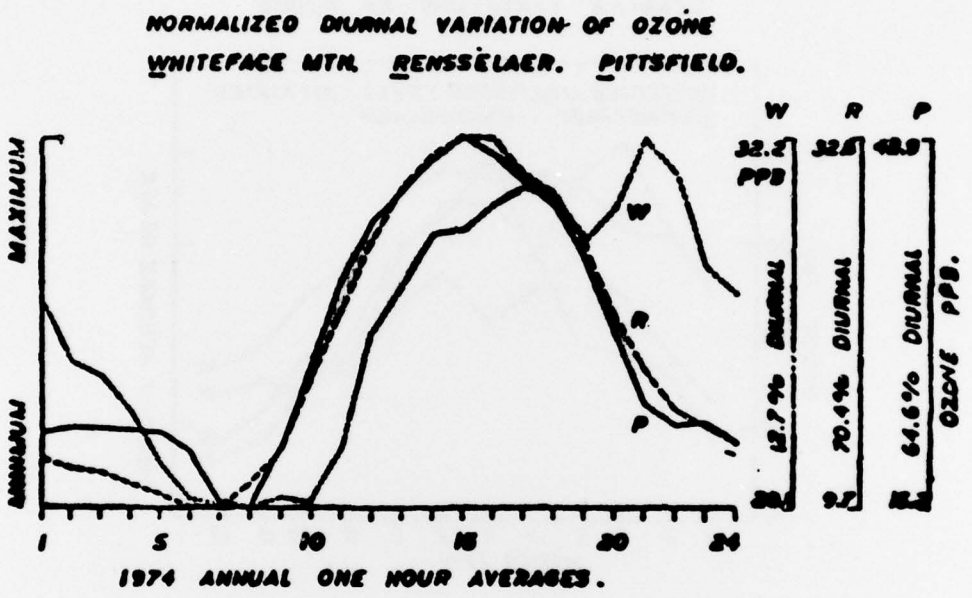
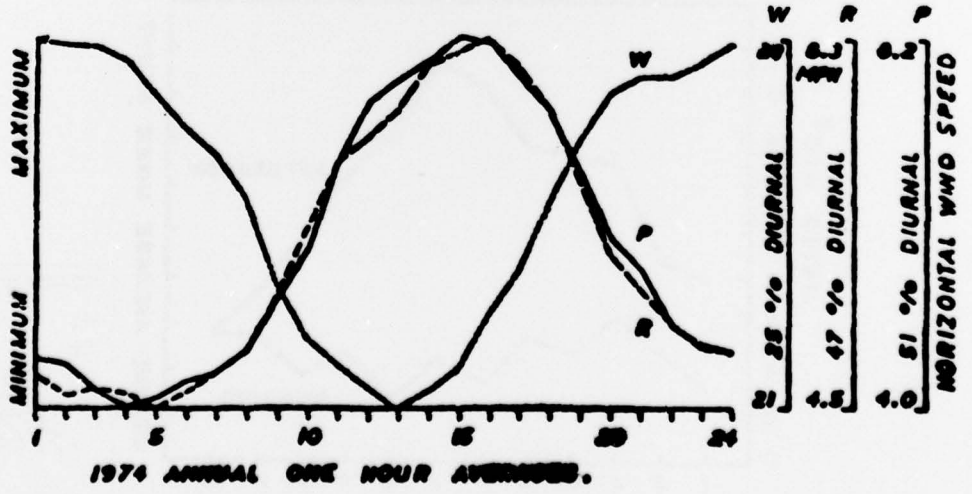
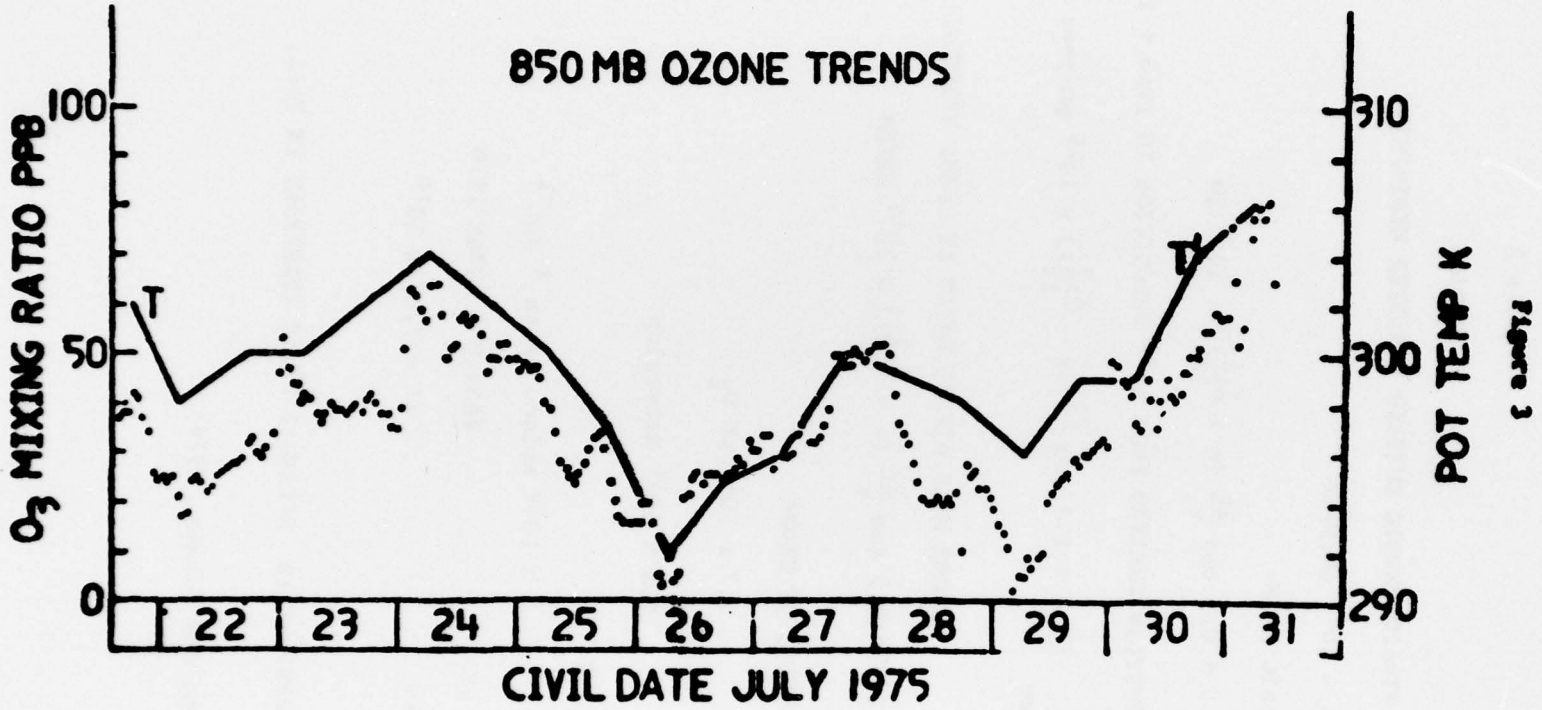


Figure 2






850 MB OZONE TRENDS
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23
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28
29
30
31
CIVIL DATE JULY 1975
310
300
290
POT TEMP K

Table 1

SUMMARY

ESTIMATED STRATOSPHERIC OUTFLOW NORTHERN HEMISPHERE

(1959) 4×10^{20} gm/year

STRATOSPHERIC MASS

$$M_s = \left[4.5 + 0.5 \cos \frac{2\pi}{\tau} \left(t - \frac{1.5}{12}\right)\right] \times 10^{20} \text{ gm}$$

(1964) OUTFLOW DERIVED FROM Sr^{90} DEPOSITION IN 1960 + 1963

$$\left(\frac{dM}{dt}\right)_{outflow} = \left[3.6 + 1.8 \cos \frac{2\pi}{\tau} \left(t - \frac{4.5}{12}\right)\right] \times 10^{20} \text{ gm/year}$$

OZONE MASS MIXING RATIO IN LOWER STRATOSPHERE

$$X_{O_3} = \left[1.3 + 0.3 \cos \frac{2\pi}{\tau} \left(t - \frac{4.5}{12}\right)\right] \times 10^{-6} \text{ gm/gm}$$

ANNUAL OUTFLOW OF OZONE

4.7×10^{14} gm O_3

5.8×10^{36} molecules

AVERAGE FLUX

7×10^{10} molecules cm^{-2} sec^{-1}

PARTZOLD 1955	FABIAN + JUNGE 1970	REGENER 1957
4×10^{10}	$(4 - 7.6) \times 10^{10}$	$(12 - 16) \times 10^{10}$

OZONE TRANSPORT IN SPRING 5 TIMES TRANSPORT IN FALL.

(Danielsen and Mohnen, 1976)